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(54) WATER PURIFICATION TREATMENT

(71) We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany, of 9 Weissfrauenstrasse, 6 Frankfurt, Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of destroying germs and algae in waters and water systems. The method effectively prevents the formation of germs and algae. It is also applicable to water which is circulated. Corrosion and skin irritation are avoided.

It is difficult to keep water such as public water supplies free from germs and algae. This also applies to cooling water systems and quite generally to circulating water systems in industrial plants.

An additional factor is that any reagents used not only have to be effective, but must also be non-corroding and must not have an irritating effect on the skin. The known substances for killing germs and combatting algae, such as oxidising agents which generate chlorine, such as chlorine, hypochlorites and organic chlorine compounds, have a strongly corroding action and very often lead to skin irritation when used in bath water.

Hydrogen peroxide or quaternary ammonium compounds, on the contrary, do not achieve the thorough killing of germs and algae which is achieved by chlorine compounds.

It has now been found that waters and water systems can be effectively freed from germs and algae, without any occurrence of corrosion, skin irritation or the formation of secondary products, even with water which are circulated, if the water or water system is treated with hydrogen peroxide and one or more quaternary ammonium compounds.

Depending on the content of germs and algae, hydrogen peroxide is generally used in a concentration of from 50 to 2000 cc per cubic metre, preferably from 50 to 150 cc per cubic metre, expressed as a 35% by weight aqueous solution. Generally there are 0.5 to 21 mols of hydrogen peroxide (100% by weight), preferably 0.5 to 1.5 mols of hydrogen peroxide (100% by weight), to 1 cubic metre of water.

Clearly other normal commercial hydrogen peroxide solutions can also be used to achieve these concentrations.

Suitable quaternary ammonium compounds are: Quaternary primary fatty amines, *e.g.* trimethyl-fatty alkyl ammonium salts, such as cetyl trimethyl ammonium chloride. Quaternary salts of tertiary amines such as *n*-alkyl benzyl ammonium salts, *e.g.* *n*-alkyl-dimethyl benzyl ammonium chlorides, such as lauryl dimethyl benzyl ammonium chloride or a mixture of n-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chlorides, or mixtures of other percentage composition or with other odd or even-numbered alkyl groups. Alkyl trimethyl ammonium chlorides, such as lauryl trimethyl ammonium chloride. Quaternary salts of ethoxylated fatty amines, such as diisobutyl phenoxyethoxy ethyl dimethyl benzyl ammonium chloride, quaternary pyridinium salts, such as lauryl or cetyl pyridinium chloride.

These quaternary ammonium compounds are generally used in quantities from 0.01 to 0.1 and preferably from 0.02 to 0.08 per litre of hydrogen peroxide (35% by weight).

The combination of hydrogen peroxide can be effected with one or more quaternary ammonium compounds. Particularly suitable is a mixture of 35% by weight hydrogen peroxide and *n*-alkyl-dimethyl benzyl ammonium chloride, and in fact a mixture containing 0.08 mol of *n*-alkyl-dimethyl benzyl ammonium chloride per litre of hydrogen peroxide solution (35% by weight), namely, the mixture of *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chlorides (referring to hereinafter as Substance 3).

A mixture which likewise proved to be effective was one comprising, per litre of 35% by weight hydrogen peroxide, 0.06 mol of *n*-alkyl-dimethyl benzyl ammonium chlorides (substance 3) and 0.02 mol of a quaternary

ammonium compound such as lauryl dimethyl benzyl ammonium chloride or lauryl pyridinium chloride. The mixture in which the lauryl compound is lauryl dimethyl benzyl ammonium chloride is referred to hereafter as " Substance 4 ".

The reagents are added in the usual manner to the water or water systems, *e.g.* by proportioning pumps or by circulation, and can be added either individually or in premixed form.

The following experiments show the superiority of the combination according to the invention over the individual action of hydrogen peroxide and the quaternary compounds, respectively.

The killing speed of the substances on *Escherichia coli, Bacterium proteus, Pseudomonas aeruginosa,* and *Staphylococcus aureus,* was investigated.

The following were used:

Substance 1 = hydrogen peroxide (35% by weight)
Substance 2 = *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethylbenzyl ammonium chloride
Substance 3 = see above
Substance 4 = see above.

All four substances were prepared in accordance with their concentration for use in bath water, *i.e.* 0.1 cc per litre of bath water, each in 4 × 100 cc of sterile, physiological common salt solution. Physiological common salt solution without additive served for control purposes.

Each solution was inoculated with 1 cc of a 24-hour broth culture of *Escheria coli, Bacterium proteus, Pseudomonas aeruginosa* or *Staphylococcus aureus,* the culture being diluted to 10^{-1}. The numbers of germs or micro-organisms was approximately 10^9 to 10^{10} germs per cc of solution.

After being kept for 1, 2, 3, 4, 5, 7.5, 10, 15, 20, 30, 60 and 120 minutes at 22° C., in each case 1 cc was removed and introduced into 15 cc of thioglycolate broth with 3% of anion-active substance and 0.3% of lecithin and phenol red as indicator.

The growth in the broth cultures was judged after incubation for 48 hours at 37° C. on the basis of the change in colour of the indicator and the clouding. The following results were obtained:

Substance 1

In the concentration in which it was added, it has a killing action on *Staphylococcus aureus* only after an active time of 120 minutes. *Escherichia coli, Bacterium proteus* and *Pseudomonas aeruginosa* even increased in number after an operating time of 120 minutes.

Substance 2

It has a bactericidal effect after 3 to 4 minutes on *Escherichia coli; Bacterium proteus* and *Pseudomonas aeruginosa* however, were not killed after an operating time of 120 minutes. On the other hand, it had a bactericidal effect on *Staphylococcus aureus* after 7½ to 10 minutes.

Substance 3

It has a bactericidal action on *Staphylococcus aureus after* 1 to 3 minutes. The combination of the two substances thus has a quicker action on this type of germ than the individual substances. *Escherichia coli* was killed by this mixture in almost the same time as by Substance 2 by itself, *i.e.* after 3 minutes. A decidedly additive effect of the mixture as compared with the separate substances was produced with *Bacterium proteus* and *Pseudomonas aeruginosa.* With both bacteria, the individual substances have no bactericidal action even after operating for 120 minutes, but the combination had a killing effect after 60 minutes.

Substance 4

The results in respect of this substance correspond to those for Substance 3, and it was only for *Bacterium proteus* that the killing time was extended from 60 to 120 minutes as compared with Substance 3.

In physiological common salt solution, all germs survived during the test period of 120 minutes.

The times for killing germs are set out in Table 1, (see below).

The experiments show that the combinations of hydrogen peroxide with quaternary compounds have a substantially quicker germ-killing action than the separate substances. It was only with the strain of *Escherichia coli,* with which the killing speed by the quaternary ammonium compounds by themselves is already very long, that the killing speed could be only shortened by an insignificant amount. Substance 3 is particularly suitable for killing the strains of bacteria which frequently occur in water.

In addition, special tests with Substance 3 show that no injury to the skin occurred. With the equicutaneous test (lobe specimen), the following solutions, diluted to the concentration of swimming bath water, was used on 17 persons undergoing the test.

Solution 1 1 litre of tap water
0.12 cc of Substance 3
Solution 2 1 litre of tap water
0.1 cc of Substance 3
Solution 3 1 litre of tap water
0.07 cc of Substance 3
Solution 4 1 litre of tap water
0.03 cc of Substance 3

Table 1

Germ-killing speeds (summary)

Substance	Killing times in minutes for:			
	Escherichia coli	*Bacterium proteus*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*
1	120	120	120	120
2	3 - 4	120	120	7.5 - 10
3	3	60	60	1 - 3
4	3	120	60	1 - 3
NaCl control	120	120	120	120

In the epicutaneous test, no changes in the skin could be detected with any of the persons undergoing the experiment after 24 to 48 hours.

Finally, Substance 3 was tested on a large-scale experiment in three different swimming pools:

1. *Indoor pool A*
Size of pool: about 100 cubic metres of water
filter plant: sand filter
water temperature: about 25 to 30°
water hardness: about 4.8 German hardness (Ullmanns Encyklopadie der technischen Chemie, (1967), p.422)
test time: from January 1970 to January 1972
pH value of the water: 7.2 to 7.6

Previously a chlorine (common salt electrolysis plant) was used. Allergic irritations led to the change-over to Substance 3.

Substance 3 was measured out as follows:

a) New charging:
about 1 litre of substance 3 per 10 cubic metres of water.
b) Obtaining the hydrogen peroxide concentration: the water is to contain about 50 to 100 cc of Substance 3 per cubic metre of water.

In practice, this was obtained with an addition of 0.3 to 0.5 litre of Substance 3 per 10 cubic metres of water every four days or 3 to 4 days, and with an average temperature of about 25° C., the water was free from germs and algae. Bacteriological investigations at certain time intervals gave no occasion for complaint.

2. *Open-air pool B*
Size of pool: about 50 cubic metres of water
filter plant: sand/silica filter
water temperature: about 23° to 28° C.
water hardness: about 5° German hardness
test time: from April to November, 1970 and 1971
pH value of the water: 7.2 to 7.6.

Although contaminations in the open-air pool were found to occur substantially more strongly than in the indoor pool, a germ-free and algae-free water could be produced with the same measured quantities as in the indoor pool A with Substance 3. Here, the addition is likewise 0.3 to 0.5 litre of Substance 3 per 10 cubic metres of water every 3 to 4 days. The pH value of the water was on average between 7.2 and 7.8. A correction with hydrochloric acid or soda was consequently superfluous. The checking of the pH value and the hydrogen peroxide concentration was carried out twice a week. There were never any complaints.

3. *Open-air pool C*
Size of pool: about 25 cubic metres of water
Filter plant: kieselguhr filter
water temperature: about 20° to 23° C.
pH value of the water: 7.3 to 7.6
test time: April-September, 1970 and 1971

With daily checking of the hydrogen peroxide concentration and the pH value, about 0.3 to 0.5 litre of Substance 3 was introduced every 3 to 4 days. It was established that this amount was sufficient to always keep the water fresh. No irritation in the region of the scalp, the eye conjunctiva or the mucus membranes was found, this being in contrast with a chlorine bleaching solution.

The technical advance of the process according to the invention thus lies in the killing of germs and algae, and in fact that it is possible to use such low concentrations of the reagents under consideration, that neither corrosion, skin irritation or other secondary phenomena occur. Furthermore, the process can also be applied to water which is circulated.

WHAT WE CLAIM IS:—

1. A process for destroying germs and algae in water and water systems, which comprises treating the water or water system with hydrogen peroxide and one or more quaternary ammonium compounds.

2. A process as claimed in Claim 1, wherein hydrogen peroxide as a 35% by weight aqueous solution is used in a quantity of from 50 to 2000 cc per cubic metre of water to be treated and the quaternary ammonium compound or compounds are used in an amount from 0.01 to 0.1 mol per litre of aqueous 35% by weight hydrogen peroxide.

3. A process as claimed in Claim 1 or 2, wherein an *n*-alkyl benzyl ammonium salt is used as the quaternary ammonium compound.

4. A process as claimed in any of Claims 1 to 3, wherein *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chloride is used as the quaternary ammonium compound.

5. A process as claimed in any of Claims 1 to 3, wherein lauryl dimethyl benzyl ammonium chloride is used as the quaternary ammonium compound.

6. A process as claimed in any of Claims 1 to 4 wherein 35% by weight aqueous hydrogen peroxide, containing 0.08 mol of *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chloride per litre is used.

7. A process as claimed in any of Claims 1 to 4 wherein 35% by weight aqueous hydro-

gen peroxide, containing 0.02 mol of *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chloride per litre is used.

8. A process as claimed in any of Claims 1 to 4 wherein 35% by weight aqueous hydrogen peroxide, containing 0.06 mol of *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chloride and 0.02 mol of lauryl dimethyl benzyl ammonium chloride per litre is used.

9. A process as claimed in any of Claims 1 to 4 wherein 35% by weight aqueous hydrogen peroxide, containing 0.06 mol of *n*-alkyl (50% C_{14}, 40% C_{12}, 10% C_{16})-dimethyl benzyl ammonium chlorides and 0.02 mol of lauryl pyridinium chloride per litre is used.

10. A process for destroying germs and algae in water and water systems as claimed in Claim 1, substantially as hereinbefore described.

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Verfahren zum Entkeimen und Entalgen von Wässern und Wassersystemen

Die Anmeldung betrifft ein Verfahren zum Entkeimen und Entalgen von Wässern und Wassersystemen, das wirksam die Bildung von Keimen und Algen verhindert - auch bei in Kreislauf geführten Wässern - und gleichzeitig Korrosionen und Hautreizungen vermeidet.

Bekanntlich ist es schwierig, Wässer wie Trink- oder Badewasser keim- und algenfrei zu halten. Das letztere gilt auch für Kühlwasser- und ganz allgemein für Kreislaufwassersysteme in industriellen Anlagen.

Es kommt hinzu, dass die betreffenden Reagenzien nicht nur wirksam, sondern auch nicht korrodierend bzw. nicht hautreizend sein dürfen. Die bekannten Stoffe zur Keimabtötung und Algenbekämpfung wie chlorabspaltende Oxidationsmittel wie Chlor, Hypochlorite, organische Chlorverbindungen wirken stark korrodierend und führen bei der Badewasseraufbereitung sehr oft zu Hautreizungen.

Wasserstoffperoxid wie auch quaternäre Ammoniumverbindungen dagegen erreichten nicht die durchgreifende Keim- und Algenabtötung wie Chlorverbindungen.

Es wurde nun gefunden, dass sich Wässer und Wassersysteme wirksam entkeimen und entalgen lassen, ohne dass Korrosionen, Hautreizungen oder die Bildung von Nebenprodukten- auch bei im Kreislauf geführten Wässern - auftreten, wenn die Wässer oder Wassersysteme mit einer Kombination aus Wasserstoffperoxid und quaternären Ammoniumverbindungen behandelt werden.